

Pyraclostrobin

Summary of Analytical Chemistry and Residue Data

DP#: 374617



**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460**

OFFICE OF PREVENTION, PESTICIDE
AND TOXIC SUBSTANCES

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

MEMORANDUM**Date:** 4/7/10

SUBJECT: **Pyraclostrobin.** Petition for New Uses and Tolerances on Alfalfa. Independent Laboratory Validation of Poultry Analytical Method and Revised Section F. Summary of Analytical Chemistry and Residue Data.

PC Code: 099100**Decision No.:** 405748**Petition No.:** 9F7528**Risk Assessment Type:** NA**TXR No.:** NA**MRID No.:** 47938901**DP Num.:** D374617**Registration No.:** 7969-186, 7969-266, and 7969-199**Regulatory Action:** Section 3 Registration**Case No.:** NA**CAS No.:** 175013-18-0**40 CFR:** 180.582

Ver. Apr. 08

FROM: W. Cutchin, Acting Senior Branch Scientist *William Cutchin*
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Risk Integration, Minor Use and Emergency Response Branch (RIMUERB)
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THROUGH: L. Cheng, Senior Chemist *Ling Cheng*
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TO: T. Kish/J. Bauzin PM 22
RD (7509P)

Executive Summary

BASF previously proposed new uses for pyraclostrobin on alfalfa as a seed treatment and as broadcast foliar applications. The ARIA review of the proposed uses (PP#9F7528, DP#367409, W. Cutchin, 10/29/09) indicated a number of deficiencies:

- The proposed a liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) tolerance enforcement method for poultry commodities (BASF Method D9902) must undergo an acceptable independent laboratory validation (ILV) and tolerance method validation (TMV) prior to being approved as an enforcement method.

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1/19/2010
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- Analytical standards for BF 500-5, BF 500-8 and BF 500-9, which are the common moiety analytes determined by the livestock commodity enforcement methods, must be submitted to the EPA National Pesticide Standards Repository.
- A revised Section F for the residues of pyraclostrobin on alfalfa forage at 10 ppm and alfalfa hay at 30 ppm is required
- Based on the calculated dietary burden for poultry and data from the poultry feeding and metabolism studies, tolerances should be established for poultry meat, fat and meat byproducts, and eggs each at 0.1 ppm. A revised Section F is required

The registrant has submitted an ILV and revised Section F. No other aspects of the original review are addressed in this memo.

Pyraclostrobin, methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl] methoxycarbamate, belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance that inhibits spore germination, mycelial growth, and sporulation of the fungi on the leaf surface. Pyraclostrobin is currently registered to BASF Corporation (BASF) for use on a wide variety of field, vegetable, fruit, and nut crops for direct foliar applications and on field and vegetable crops as a seed treatment. It is formulated as water-dispersible granules (WDG), emulsifiable concentrates (EC), or suspension concentrates (SC = FIC). For field uses, pyraclostrobin is typically applied as foliar applications using ground or aerial equipment at maximum seasonal rates of 0.3-3.0 lb ai/A.

Pyraclostrobin tolerances for plant commodities are listed in 40 CFR §180.582 (a)(1) and are expressed in terms of the combined residues of the pyraclostrobin and its desmethoxy metabolite BF 500-3 (methyl N-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl carbamate), expressed as parent compound. The established tolerances for plant commodities range from 0.02 ppm in/on wheat grain to 30 ppm in/on cotton gin byproducts. Tolerances for pyraclostrobin in livestock commodities are listed in 40 CFR §180.582 (a)(2) and are expressed in terms of the combined residues of the pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1*H*-pyrazol-3-ol (BF 500-5) and 1-(4-chloro-2-hydroxyphenyl)-1*H*-pyrazol-3-ol (BF 500-8), expressed as parent compound. The established tolerances for livestock commodities range from 0.1 to 1.5 ppm; no tolerances are established for poultry commodities.

The submitted ILV is adequate. The independent laboratory indicated that no significant modifications were made to the method. The validated method limit of quantitation (LOQ) for combined BF 500-5 and BF 500-9 residues, in parent equivalents, is 0.1 ppm in eggs and poultry tissues. ARIA has determined that BASF Method D9902, a liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) method similar to the existing enforcement method for ruminants is adequate for enforcement purposes for residues of pyraclostrobin on poultry commodities. A copy of the method will be forwarded to FDA.

As of 3/17/10 the required standards of the pyraclostrobin metabolites BF 500-5, BF 500-8 and BF 500-9 have not been submitted. This remains a deficiency for this petition.

The submitted revision to Section F fulfills the requested additions indicated by ARIA's previous review.

Regulatory Recommendations and Residue Chemistry Deficiencies

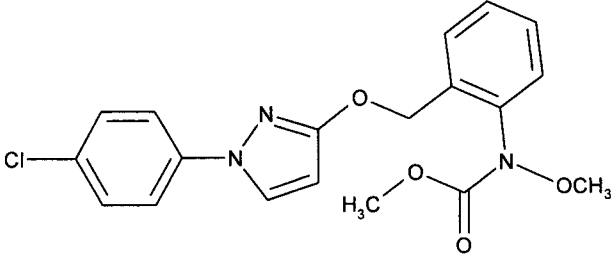
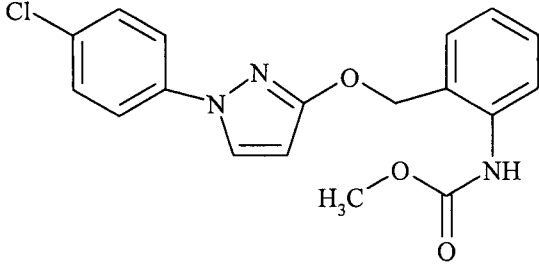
Pending receipt of the metabolite standards, ARIA recommends for establishing new pyraclostrobin tolerances at 10 ppm on alfalfa forage, 30 ppm on alfalfa hay, and poultry meat, fat and meat byproducts, and eggs each at 0.1 ppm.

Since a human health risk assessment has been conducted using the tolerances noted above (PP#9F7528, DP#362855, W. Cutchin, 11/19/09), a revised risk assessment would not be required upon receipt of the analytical standards and the resolution of the other deficiencies noted in the assessment.

Note to PM: The required changes in the CFR tolerance expressions for pyraclostrobin described in the last ARIA document should be implemented.

Background

Pyraclostrobin belongs to the strobilurin class of fungicides, which are synthetic analogs of a natural antifungal substance which inhibits spore germination and inhibits mycelial growth and sporulation of the fungus on the leaf surface.

TABLE 1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.	
Compound	
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
Molecule weight	387.8
IUPAC name	methyl <i>N</i> -{2-[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yloxy]methyl}phenyl <i>N</i> -methoxy carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use product (EPs)	12.8% WDG (Pristine® Fungicide; EPA Reg. No. 7969-199; also contains 25.2% boscalid) 1.67 lb/gal EC (Stamina™ Fungicide Seed Treatment; EPA Reg. No. 7969-266) 2.09 lb/gal EC (Headline® Fungicide; EPA Reg. No. 7969-186)
Regulated plant metabolite	
Common name	pyraclostrobin desmethoxy metabolite

Pyraclostrobin

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TABLE 1. Nomenclature of Pyraclostrobin and its Desmethoxy Metabolite.

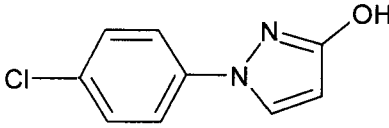
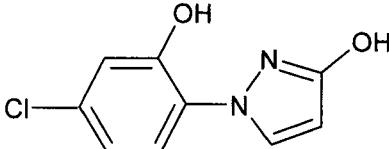
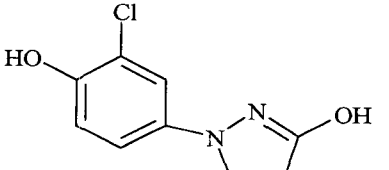
Company experimental name	BF 500-3
Molecular weight	357.8
Chemical name	Methyl-N-[[[1-(4-chlorophenyl) pyrazol-3-yl]oxy]o-tolyl] carbamate

TABLE 2. Physicochemical Properties of Technical Grade Pyraclostrobin.

Parameter	Value	References ¹
Melting point/range	63.7-65.2°C	D269848 & D274191
pH	Not reported	D269848 & D274191
Density	1.285 g/cm ³ at 20°C	D269848 & D274191
Water solubility at 20°C	2.41 mg/L (deionized water) 1.9 mg/L (pH 7) 2.3 mg/L (pH 4) 1.9 mg/L (pH 9)	D269848 & D274191
Solvent solubility (g/100 mL at 20°C)	acetone 16-20 ethyl acetate 6.7-8.0 methanol 4-5 2-propanol <0.01 acetonitrile 4-5 dichloromethane 20-25 toluene 2-5 n-heptane <0.01 1-octanol <0.01 olive oil 2.9 N,N-DMF >25	D269848 & D274191
Vapor pressure	2.6 x 10 ⁻¹⁰ hPa at 20°C 6.4 x 10 ⁻¹⁰ hPa at 25°C	D269848 & D274191
Dissociation constant, pK _a	Does not dissociate in water.	D269848 & D274191
Octanol/water partition coefficient, Log(K _{OW}) at room temperature	3.80 at pH 6.2 4.18 at pH 6.5	D269848 & D274191
UV/visible absorption spectrum	λ_{\max} = 275 nm	D269848

¹ Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and D274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

TABLE 3. Chemical Structures of Pyraclostrobin Metabolites

Metabolites	Structure
BAS 500-5 1-(4-chlorophenyl)-1H-pyrazol-3-ol	
BAS 500-8 1-(4-chloro-2-hydroxyphenyl)-1H-pyrazol-3-ol	
BAS 500-9 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol	

860.1340 Residue Analytical Methods

PP#9F7528, DP#367409, W. Cutchin, 10/29/09

Animal commodities: Two tolerance enforcement methods have been proposed for ruminant commodities. One is an HPLC/UV method 439/0, which determines residues of pyraclostrobin *per se*, and Method 446, which consists of a gas chromatography with mass spectroscopy detector (GC/MS) Method 446/0 and LC/MS/MS Method 446/1. Method 446 includes a hydrolysis step, and determines residues of pyraclostrobin and its metabolites as BF 500-5 and BF 500-8. The validated method LOQs for BF 500-5 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues, and the validated LOQs for BF 500-8 type residues, in parent equivalents, are 0.01 ppm for milk and 0.05 ppm for tissues. Independent method validation data for the HPLC/UV and LC/MS/MS methods are acceptable. Radiovalidation data submitted for the GC/MS and LC/MS/MS methods are adequate for liver and milk, and marginal for muscle. Method 446 has been forwarded to ACB/BEAD for petition method validation. However, following the SOP (ACB-019) for reviewing tolerance methods (September 15, 2008), HED has determined that Method 446 is suitable as an enforcement method (PP#s 8F7385, 8F7390, and 8E7394; DP Num 343700; B. O'Keefe; 9/7/07).

For enforcing tolerances on poultry commodities, BASF has purposed use of a LC/MS/MS Method D9902, which is similar to the method for ruminant commodities (LC/MS/MS Method 446/1). Method D9902 is also a common moiety method that includes a base hydrolysis step. The principle difference between the two methods is that Method D9902 determines residues of pyraclostrobin and its metabolites convertible to BF 500-5 or BF 500-9. BF 500-9 is an isomer of BF 500-8, in which the hydroxyl group is at a different position on the chlorophenyl ring. Adequate method validation data have been provided for Method D9902, and the validated LOQ for each analyte is 0.05 ppm in eggs and poultry tissues, for a combined LOQ of 0.1 ppm. All residues are expressed in parent equivalents. This method was used for data collection in the poultry feeding study. Separate radiovalidation data are not required for Method D9902, as adequate radiovalidation data are available for Method 446/1 which uses similar sample extraction and purification procedures.

BASF has now submitted an ILV ((MRID 47938901). The independent laboratory indicated that the sponsor was not contacted during the study and that no significant modifications were made to the analytical method. The validated method LOQ for combined BF 500-5 and BF 500-9 residues, in parent equivalents, is 0.1 ppm in eggs and poultry tissues.

Conclusion: ARIA has determined that BASF Method D9902, a LC/MS/MS method similar to the existing enforcement method for ruminants is adequate for enforcement purposes for residues of pyraclostrobin on poultry commodities. A copy will be forwarded to FDA.

860.1480 Meat, Milk, Poultry, and Eggs

PP#0F6139; DP# 269668, 11/28/01, L. Cheng
PP#9F7528, DP#367409, W. Cutchin, 10/29/09

Adequate cattle and poultry feeding studies are available. The current tolerances for livestock commodities are based on the residue data from the cattle and poultry feeding studies and the

previously calculated dietary burdens of livestock for pyraclostrobin. The maximum dietary burdens for livestock were originally calculated to be 36.3 ppm for beef cattle, 35.4 ppm for dairy cattle, and 0.35 ppm for poultry. Most recently, the dietary burdens for livestock were calculated to be 4.9 ppm for beef cattle, 9.5 ppm for dairy cattle, 0.545 ppm for swine, and 0.945 ppm for poultry (DP# 359194, M. Negussie, 4/02/09).

As alfalfa forage and hay are major livestock feedstuffs, the dietary burdens for livestock were recalculated for this petition. Based on the recent changes in calculating residues in reasonably balanced livestock diets (ChemSAC memo, 6/30/08), the dietary burden for livestock to pyraclostrobin residues was recalculated to be 6.1 ppm for beef cattle, 12.9 ppm for dairy cattle, 2.6 ppm for poultry, and 2.1 ppm for swine (e-mail, J. Stokes, 10/7/09; Table 3).

TABLE 3. Calculation of Maximum Reasonably Balanced Dietary Burdens of Pyraclostrobin Residues for Livestock.

Feedstuff	Type	% Dry Matter	% Diet	Tolerance (ppm)	Dietary Contribution (ppm)
Poultry CC 75%, PC 25%					
Barley, grain	CC	88	75	1.4	1.05
Canola/sunflower, meal	PC	92	20	0.3	0.06
Alfalfa, meal	PC	89	5	30	1.5
TOTAL BURDEN	--	--	100	--	2.6

Poultry feeding study. Three groups of laying hens (4 hens per subgroup with 3-5 subgroups/dose) were orally dosed once daily for 30 consecutive days with pyraclostrobin at dose levels equivalent to 0.28, 0.88 and 3.01 ppm in their diet. These dose levels are respectively equivalent to 0.1x, 0.3x, and 1.1x the currently calculated dietary burden for poultry.

For the high-dose group (1.1x dietary burden) residues of pyraclostrobin and its metabolites hydrolyzable to BF 500-5 were less than the method LOQ (<0.05 ppm) in all egg and tissue samples, except for one egg sample (Day 17), where residues of pyraclostrobin were detected at 0.064 ppm. However, upon reanalysis, pyraclostrobin residues in this egg sample were <0.05 ppm. Residue analysis of BF 500-8 was not conducted as the metabolism data show all metabolites hydrolyzable to BF 500-8 would be less than 10% of the total radioactive residues (TRR). Instead an isomeric compound (BF 500-9) was measured, and all residues of BF 500-9 were <0.05 ppm in all egg and tissue samples.

Based on the recalculated dietary burden for poultry (2.6 ppm), the high-dose group in the poultry feeding study is now considered to be equivalent to 1.1x the poultry dietary burden. The combined residues of pyraclostrobin and its metabolites convertible to BF 500-5 and BF 500-9 were <LOQ in eggs and all tissues; however, because there is no dose group in the feeding study representing a 10x feeding level, ARIA can no longer verify that residues in poultry commodities represent a Category 180.6(a)(3) situation.

To further assess the need for tolerances, ARIA and HED re-examined the data from the poultry metabolism studies, in which hens were dosed at levels equivalent to 12.1-12.7 ppm in the diet (~4.8x dietary burden) for 7 consecutive days. For poultry fat and liver, which had TRRs of 0.065-0.083 ppm and 0.317-0.474 ppm respectively, the identified residues of pyraclostrobin and its metabolites potentially convertible to BF 500-5 or BF 500-9 were totaled for both matrices.

At dose levels equivalent to ~4.8x the poultry dietary burden, combined pyraclostrobin residues were estimated to be 0.041-0.042 ppm in fat and 0.082-0.143 ppm in liver. When extrapolated to a 10x feeding level, combined residues could be 0.088ppm in fat and 0.299 ppm in liver. As the combined residues of concern could be at or above the method LOQ (0.1 ppm) in the poultry fat and liver following only 7 days of dosing at a 10x level, it is not possible to establish with certainty whether finite residues will be incurred in poultry fat and meat byproduct, but there is a reasonable expectation of finite residues. Therefore, tolerances should be established for poultry fat and meat byproducts at the proposed enforcement method LOQ (0.1 ppm).

The levels of the TRR in muscle were ≤ 0.009 ppm and in eggs were ≤ 0.037 ppm at a ~4.8x feeding level. Considering the levels of the TRR levels in muscle (≤ 0.009 ppm) and eggs (≤ 0.037 ppm) at a ~4.8x feeding level, quantifiable levels (≥ 0.1 ppm) of the residues of concern would normally not be expected to occur in eggs and poultry meat at a 10x feeding level. However, as the poultry metabolism study was only conducted for 7 days and the TRRs may not have reached a plateau, it is not possible to establish with certainty whether finite residues will not be incurred in poultry meat and eggs. Therefore, tolerances for egg and poultry meat should be established at the proposed enforcement method LOQ (0.1 ppm).

BASF has submitted a revised Section F for the residues of pyraclostrobin on poultry meat, fat and meat byproducts, and eggs at 0.1 ppm.

Conclusion: The submitted revision to Section F fulfills the requested additions indicated by ARIA's previous review.

860.1500 Crop Field Trials

MRID 47584401, W. Cutchin, 10/29/09
PP#9F7528, DP#367409, W. Cutchin, 10/29/09

BASF submitted field trial data on alfalfa in support of a new use for pyraclostrobin (EC) on alfalfa. Twelve alfalfa field trials were conducted in the United States in Zones 1, 2, 5, 7, 9, 10, and 11 and Canada in Zones 5 and 5B during the 2007 growing season. Each test site included one control plot and four treated plots (Treatments #2-5) that varied the number of pyraclostrobin applications (2 or 3) and the treatment to harvest intervals (14 or 21 days). For Treatments #2 and #3, pyraclostrobin (12.8% WDG) was applied to alfalfa as three broadcast foliar applications during vegetative development at rates of 0.142-0.161 lb ai/A, for total rates of 0.44-0.47 lb ai/A. For Treatment #2, the targeted timings for the three applications were 28 and 14 days before the 1st cutting and 14 days before the 2nd cutting. For Treatment #3, the targeted timings for the three applications were 35 and 21 days before the 1st cutting and 21 days before the 2nd cutting. The two RTIs were 12-15 days and 28-53 days for Treatment #2 and 13-14 days and 29-53 days for Treatment #3. For Treatments #4 and #5, pyraclostrobin (12.8% WDG) was applied to alfalfa as two broadcast foliar applications during vegetative development at rates of 0.141-0.163 lb ai/A and RTIs of 28-53 days, for total rates of 0.29-0.31 lb ai/A. The targeted timings for the two applications were 14 days before the 1st and 2nd cuttings for Treatment #4 and 21 days before the 1st and 2nd cuttings for Treatment #5. All applications were made using ground equipment at volumes of 20-34 gal/A, and included the use of adjuvants.

With the exception of one test site, three cuttings of alfalfa were harvested from each plot according to typical agricultural practices, with the 3rd cutting being made at normal maturity (beginning bloom stage). The exact treatment-to-harvest intervals for each cutting are presented below along with the residue levels in forage and hay. At each cutting, single control and duplicate treated samples of alfalfa forage and hay were collected from each test, with hay samples being field-dried to a moisture content of ~10-20% prior to sampling. After sampling, forage and hay samples were held in frozen (<-5°C) storage for up to 13 months prior to extraction for analysis. This duration is supported by the available storage stability data.

Samples of alfalfa forage and hay were analyzed for residues of pyraclostrobin and its desmethoxy metabolite BF 500-3 using an adequate LC/MS/MS method (BASF Method D9908). The validated LOQ is 0.02 ppm for each analyte in forage and hay, and the LOQ for combined residues is 0.04 ppm.

For Treatment #2 (3 applications each at ~0.15 lb ai/A with ~14-day PHI), combined residues of pyraclostrobin and BF 500-3 in/on forage were 0.44-7.24 ppm at 12-15 days after the second application (1st cutting), 0.85-8.15 ppm at 12-16 days after the third application (2nd cutting), and <0.04-0.24 ppm at 43-73 days after the third application (3rd cutting). Combined residues in/on hay were 1.42-20.49 ppm at 12-15 days after the second application (1st cutting), 4.02-22.87 ppm at 12-16 days after the third application (2nd cutting), and 0.05-0.87 ppm at 43-73 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.99, 2.69 and 0.09 ppm in/on forage and 7.84, 9.28 and 0.27 ppm in/on hay.

For Treatment #3 (3 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were 0.06-3.38 ppm at 19-23 days after the second application (1st cutting), 0.30-2.59 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.18 ppm at 49-76 days after the third application (3rd cutting). Combined residues in/on hay were 0.08-18.75 ppm at 19-23 days after the second application (1st cutting), 1.31-8.01 ppm at 20-23 days after the third application (2nd cutting), and <0.04-0.59 ppm at 49-76 days after the third application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.89, 1.15 and 0.08 ppm in/on forage and 3.44, 3.57 and 0.20 ppm in/on hay.

For Treatment #4 (2 applications each at ~0.15 lb ai/A with ~14-day PHI), combined pyraclostrobin residues in/on forage were 0.40-5.94 ppm at 12-15 days after the first application (1st cutting), 0.57-6.56 ppm at 12-16 days after the second application (2nd cutting), and <0.04-0.18 ppm at 43-70 days after the second application (3rd cutting). Combined residues in/on hay were 1.28-15.83 ppm at 12-15 days after the first application (1st cutting), 2.77-18.81 ppm at 12-16 days after the second application (2nd cutting), and 0.05-0.46 ppm at 43-70 days after the second application (3rd cutting). For the 1st, 2nd, and 3rd cuttings, combined residues respectively averaged 2.31, 2.65 and 0.08 ppm in/on forage and 7.44, 8.59 and 0.18 ppm in/on hay.

For Treatment #5 (2 applications each at ~0.15 lb ai/A with ~21-day PHI), combined residues in/on forage were <0.04-3.03 ppm at 19-23 days after the first application (1st cutting), 0.23-2.87 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.20 ppm at 49-76 days after the second application (3rd cutting). Combined residues in/on hay were 0.20-10.48 ppm at 19-23 days after the first application (1st cutting), 1.47-12.21 ppm at 20-23 days after the second application (2nd cutting), and <0.04-0.56 ppm at 46-76 days after the second application (3rd cutting).

cutting). For the 1st, 2nd, and 3rd cuttings, combined pyraclostrobin residues respectively averaged 0.80, 1.12 and 0.08 ppm in/on forage and 2.61, 3.90 and 0.20 ppm in/on hay.

Overall, combined pyraclostrobin residues were higher in forage and hay from the treatments using 3 applications rather than 2 applications, and the residues were higher in forage and hay from treatments having the ~14-day PHI rather than the ~21-day PHI. The worse-case treatment was Treatment #2, and the highest residues in forage and hay were found in the 1st and 2nd cuttings. For Treatment #2, average combined residues from the 1st and 2nd cuttings were 2.99 and 2.69 ppm for forage and 7.84 and 9.28 ppm for hay.

TABLE 4. Summary of Combined Residue Data from Alfalfa Field Trials with Pyraclostrobin (WDG).											
Commodity	Total Applic. Rate (lb ai/A)	Trt. No. ¹	Cutting	PHI (days)	Combined Residue Levels (ppm) ²						
					n	Min.	Max.	HAFT ³	Median	Mean	Std. Dev.
Alfalfa (proposed use = 0.44 lb ai/A total application rate, 14-day PHI)											
Alfalfa Forage	0.44-0.47	2 ⁴	1 st	12-15	24	0.44	7.24	6.69	2.07	2.99	2.02
			2 nd	12-16	24	0.85	8.15	7.41	1.55	2.69	1.97
			3 rd	43-73	22	<0.04	0.24	0.21	0.07	0.09	0.06
	0.45-0.47	3	1 st	19-23	24	0.06	3.38	3.21	0.79	0.89	0.81
			2 nd	20-23	24	0.30	2.59	2.47	0.97	1.15	0.72
			3 rd	49-76	22	<0.04	0.18	0.18	0.06	0.08	0.04
	0.29-0.31	4	1 st	12-15	24	0.40	5.94	5.35	1.91	2.31	1.56
			2 nd	12-16	24	0.57	6.56	6.42	1.97	2.65	1.77
			3 rd	43-70	22	<0.04	0.18	0.18	0.05	0.08	0.05
	0.30-0.31	5	1 st	19-23	24	<0.04	3.03	3.00	0.67	0.80	0.79
			2 nd	20-23	24	0.23	2.87	2.78	1.03	1.12	0.63
			3 rd	49-76	22	<0.04	0.20	0.20	0.05	0.08	0.05
Alfalfa Hay	0.44-0.47	2 ⁴	1 st	12-15	24	1.42	20.49	19.77	6.60	7.84	5.27
			2 nd	12-16	24	4.02	22.87	22.19	7.07	9.28	5.47
			3 rd	43-73	22	0.05	0.87	0.64	0.22	0.27	0.23
	0.45-0.47	3	1 st	19-23	24	0.08	18.75	16.87	2.27	3.44	4.45
			2 nd	20-23	24	1.31	8.01	7.72	3.56	3.57	1.89
			3 rd	49-76	22	<0.04	0.59	0.52	0.15	0.20	0.18
	0.29-0.31	4	1 st	12-15	24	1.28	15.83	15.28	6.37	7.44	4.44
			2 nd	12-16	24	2.77	18.81	17.93	7.86	8.59	4.51
			3 rd	43-70	22	0.05	0.46	0.42	0.12	0.18	0.13
	0.30-0.31	5	1 st	19-23	24	0.20	10.48	9.88	1.72	2.61	2.80
			2 nd	20-23	24	1.47	12.21	10.70	3.18	3.90	2.34
			3 rd	49-76	22	<0.04	0.56	0.51	0.13	0.20	0.17

¹ Treatments #2 and #3 included three pyraclostrobin applications at ~0.145 lb ai/A/application with the first and second applications made prior to the 1st cutting and the final application made prior to the 2nd cutting. Treatments #4 and #5 included two applications at ~0.145 lb ai/A/application, with the first application made prior to the 1st cutting and the second application made prior to the 2nd cutting.

² The combined LOQ for residues of pyraclostrobin and BF 500-3 is 0.04 ppm. For purposes of calculating median and mean and standard deviation, the LOQ (0.04 ppm) was used for residue values <LOQ.

³ HAFT = Highest Average Field Trial.

⁴ The residue data used to calculate tolerances for forage and hay are **bolded**.

Although no field trial data were submitted reflecting use of the proposed EC formulation, previously submitted side-by-side field trials on tomatoes, cucumbers, and grapes comparing WDG and EC formulations of pyraclostrobin have shown that residues resulting from the two types of formulations are similar (DP# 269668, L. Cheng, 11/28/01). Therefore, the available data for the WDG formulation will also cover the use of the EC formulations on alfalfa.

Field trial data were not submitted to support the proposed seed treatment use on alfalfa; however, no seed treatment residue data are required as the seed treatment rate is negligible compared to the proposed foliar applications. Based on typical seeding rates for alfalfa (2-20 lb seed/A), the maximum seed treatment rate (0.04 lb ai/100 lb seed) would be equivalent to a field use rate of 0.008 lb ai/A, compared to the maximum foliar rate of 0.44 lb ai/A.

The submitted alfalfa field trial data are adequate and will support the use of pyraclostrobin, formulated as a WDG, for foliar applications to alfalfa. An adequate number of tests were conducted on alfalfa in the appropriate geographic regions, and the tests were conducted at ~1x the proposed use rate. Samples were collected around the proposed PHI and analyzed for residues of both parent and metabolite BF 500-3 using an adequate LC/MS/MS method. The field trial data are also supported by the available storage stability data. The available field trial data support tolerances of 10 ppm for alfalfa forage and 30 ppm for alfalfa hay.

BASF has submitted a revised Section F for the residues of pyraclostrobin on alfalfa forage at 10 ppm and hay at 30 ppm.

Conclusion: The submitted revision to Section F fulfills the requested additions indicated by ARIA's previous review.

860.1650 Submittal of Analytical Reference Standards

Analytical reference standards for pyraclostrobin (with an expiration date of 2/1/10) and its desmethoxy metabolite (with an expiration date of 11/1/11) are currently available in the EPA National Pesticide Standards Repository (personal communication with Dallas Wright; ACB/BEAD; 7/22/09). However, analytical standards are not currently available for the common moiety analytes (BF 500-5, BF 500-8 and BF 500-9) determined by the tolerance enforcement methods for animal commodities (email, C. Stafford, 3/17/10). **Analytical reference standards for these three analytes must be supplied and supplies replenished as requested by the Repository.** The reference standards should be sent to the Analytical Chemistry Lab, which is located at Fort Meade, to the attention of either Theresa Cole or Frederic Siegelman at the following address:

USEPA
National Pesticide Standards Repository/Analytical Chemistry Branch/OPP
701 Mapes Road
Fort George G. Meade, MD 20755-5350

(Note that the mail will be returned if the extended zip code is not used.)

Conclusion: This deficiency remains outstanding for this action.

Pyraclostrobin

Summary of Analytical Chemistry and Residue Data

DP#: 374617

TABLE 5. Tolerance Summary for Pyraclostrobin.			
Commodity	Proposed/ Established Tolerance (ppm)	Recommended Tolerance (ppm)	Comments; <i>Correct Commodity Definition</i>
40 CFR 180.582(a)(1)			
Alfalfa, Forage	10	10	Adequate alfalfa forage and hay residue data are available. The tolerances were calculated using the tolerance harmonization spreadsheet and the residue data from the 1 st and 2 nd cuttings of Treatment #2.
Alfalfa, Hay	30	30	
40 CFR 180.582(a)(3) ¹			
Poultry, fat	0.1	0.1	Based on the calculated dietary burden for poultry and the data from the poultry feeding and metabolism studies, tolerances are required at the method LOQ.
Poultry, meat byproducts	0.1	0.1	
Poultry, meat	0.1	0.1	
Eggs	0.1	0.1	

¹ For poultry commodities, tolerances should be expressed as the combined residues of the pyraclostrobin and its metabolites convertible to 1-(4-chlorophenyl)-1H-pyrazol-3-ol (BF 500-5) and 1-(3-chloro-4-hydroxyphenyl)-1H-pyrazol-3-ol (BF 500-9), expressed as parent compound.

References

DP Number: 367409
 Subject: PP#9F7528, Pyraclostrobin. Petition for New Uses and Tolerances on Alfalfa.
 Summary of Analytical Chemistry and Residue Data.
 From: W. Cutchin
 To: T. Kish/J. Bauzin PM 22
 Dated: 10/29/09
 MRIDs: 47584401

Pyraclostrobin

Summary of Analytical Chemistry and Residue Data

DP#: 374617

DP Numbers: 269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429

Subject: PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data.

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 11/28/01

MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

DP Numbers: 281042, 286732, 287729, 288459, 290342, 290343, 290369, 292440, 293088, 293684, 295893, and 298178

Subject: Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, *Brassica* leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical Chemistry and Residue Data..

From: L. Cheng

To: C. Giles-Parker/J. Bazuin

Dated: 7/26/04

MRIDs: 45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102